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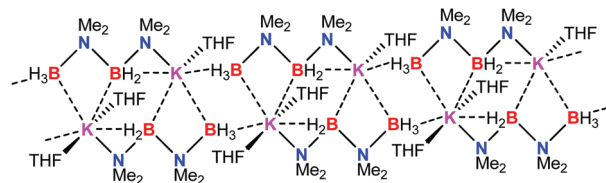
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Alkali metal-mediated dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$

Peter Bellham, Michael S. Hill* and
Gabriele Kociok-Köhn

Bis(trimethylsilyl)amide derivatives of the group 1 elements (Li, Na, K) are competent pre-catalysts for the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ via the formation of intermediates containing $[\text{H}_3\text{BNMe}_2\text{BH}_2\text{Me}_2\text{N}]^-$ anions.



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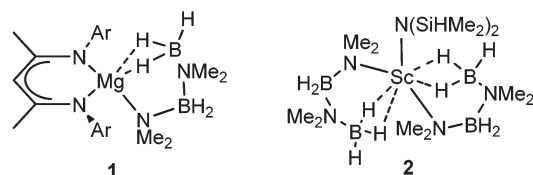
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Peter Bellham, Michael S. Hill* and Gabriele Kociok-Köhn

Bis(trimethylsilyl)amide derivatives of the group 1 elements (Li, Na, K) are competent pre-catalysts for the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ via the formation of intermediates containing $[\text{H}_3\text{BNMe}_2\text{BH}_2\text{Me}_2\text{N}]^-$ anions.

The last 10 years have overseen considerable interest in the reactivity of ammonia borane (AB) and, more generally, amine boranes due to their potential use as chemical storage media for hydrogen fuel.¹ While initial gas evolution from AB occurs at $>120^\circ\text{C}$, temperatures in excess of 1200°C are required to release the final equivalent of hydrogen. These impractically energetic conditions have, thus, prompted considerable interest in both metallated amidoborane species and the development of catalytic means to effect H_2 elimination.² Isolable derivatives of the elements from groups 1 and 2 have attracted particular attention with systems derived from lithium and the alkaline earth metals magnesium, calcium and strontium displaying significantly reduced onset H_2 evolution temperatures in comparison to pure AB.³

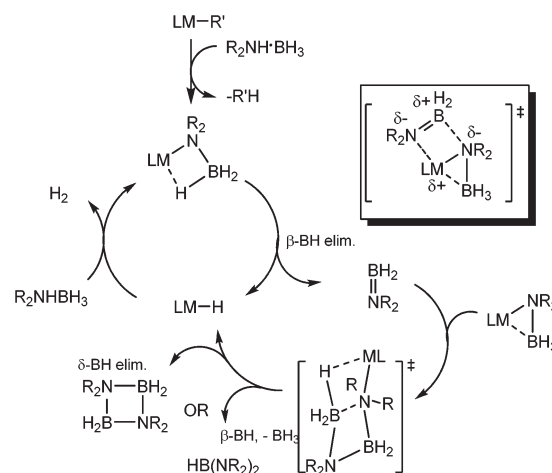


Ar = 2,6-di-iso-propylphenyl

While many transition metal-derived catalysts have now been reported to effect AB and amine borane dehydrocoupling,⁴ a majority of these systems are proposed to occur *via* processes involving redox changes at the metal centre. In contrast, non-redox-based catalysis is represented by a comparably limited number of d^0 species derived from the early transition metals

of groups 3–5 and aluminium and gallium in group 13.^{5,6} Our own work has concentrated on the reactivity of similarly d^0 complexes of magnesium and calcium amides and alkyls with secondary amine boranes, $\text{R}_2\text{NH}\cdot\text{BH}_3$.⁷ In such cases the formation of the ultimate products of dehydrocoupling, cyclic borazanes of the form $[\text{R}_2\text{NBH}_2]_2$, are found to be produced through the formation of isolable compounds containing co-ordinated $[\text{H}_3\text{BNR}_2\text{BH}_2\text{R}_2\text{N}]^-$ anions (for example, compounds 1 and 2).

To account for these observations we have suggested that this process is predominantly metal-mediated and dependent upon the mechanism illustrated in Scheme 1,⁷ for which some supporting evidence has recently emerged from computational DFT studies.⁸ Under this regime, the primary B–N bond forming reaction requires a sequence of metallated amidoborane β -hydride elimination and polarised $\text{R}_2\text{N}=\text{BH}_2$ insertion and δ -hydride elimination steps. We have proposed that this latter reaction occurs through the intermediacy of species similar to 1 and 2 and that the kinetic facility for this reaction



Scheme 1 Suggested mechanism for the group 2-centred dehydrocoupling of secondary amine boranes, $\text{R}_2\text{NH}\cdot\text{BH}_3$ (R = alkyl).

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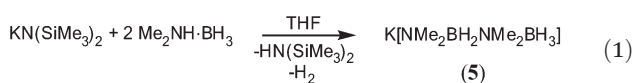
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[†] Electronic supplementary information (ESI) available. CCDC 1043568. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00178a

is dictated by the charge density and resultant ability of the M^{2+} centre to polarise and activate a B–H bond of the ligated $[H_3BNR_2BH_2R_2N]^-$ anion, such that the dehydrocoupling activity describes a reactivity trend $Mg > Ca > Sr > Ba$.⁷ Although the parent sodium amidoborane was reported as early as 1938 and more recent research has investigated $[LiNH_2BH_3]$ as a hydrogen storage material,⁹ we are not aware of any report of use of an alkali metal compound to mediate the *catalytic* dehydrocoupling of a representative amine borane. Notably, Sneddon has reported $[Na\{N(SiMe_3)_2\}]$ as a convenient soluble reagent for the formation of five-membered, linear aminoborane anions $Na^+[BH_3N(R)HBH_2N(R)HBH_3]^-$.¹⁰ In this contribution, therefore, we extend our studies to the group 1 (Li, Na and K) bis(trimethylsilyl)amides and provide an initial appraisal of the ability of this series of M^+ cations to mediate the dehydrocoupling of the secondary amine borane, $Me_2NH \cdot BH_3$.

More recent interest in hydrogen storage is pre-dated by over 30 years by Keller's investigation of the reactivity of group 1 reagents with a variety of borane molecules, including dimethylamine borane.^{11–17} The synthesis and solid-state structures of $[Li(NMe_2BH_3)]$ (3) and $[K(NMe_2BH_3)]$ (4) have also recently been described through syntheses employing stoichiometric reactions of $Me_2NH \cdot BH_3$ with *n*-butyl-lithium or the appropriate metal hydride.^{17,18} Although compound 3 has also been utilised as an intermediate in the synthesis of amine borane derivatives of less electropositive metals, the synthesis of these compounds is commonly frustrated by their apparent instability in ethereal solvents. Isolated samples of both 3 and 4 have been described to include up to 40% of an impurity, which is observed as unassigned triplet and quartet resonances in the ^{11}B NMR spectra.¹⁸ Although such species have not been definitively identified, Keller has also reported that the formation of 4, through the reaction of KH with dimethylamine borane, takes place *via* a metallated intermediate $[NMe_2BH_2NMe_2BH_3]^-$ anion which is unstable in the presence of excess metal hydride.^{12,14}

In an effort to resolve these observations we, thus, carried out a study of the reactivity of dimethylamine borane with the group 1 bis(trimethylsilyl)amides, $MN(SiMe_3)_2$ ($M = Li, Na, K$). These reagents were selected in preference to the group 1 hydrides due to their greater solubility in organic media and their greater purity which ensured that accurate stoichiometric quantities of the alkali metal reagent could be reacted with the amine borane. An initial reaction between $[K\{N(SiMe_3)_2\}]$ and two equivalents of $Me_2NH \cdot BH_3$ at room temperature was, thus, undertaken and found to result in the clean formation of Keller's previously described $[K\{NMe_2BH_2NMe_2BH_3\}]$ derivative (5) (eqn (1)).



The ^{11}B NMR spectrum of 5 at room temperature comprised two broad, unresolved resonances at $\delta = -12.3$ ppm and $\delta = 2.6$ ppm, assigned to the BH_3 and BH_2 units of a potassium co-

ordinated $[NMe_2BH_2NMe_2BH_3]^-$ anion respectively, which did not display any resolvable $^1J_{BH}$ coupling even at reduced temperature. Although this ^{11}B NMR chemical shift data is comparable with those of the homoleptic magnesium complex $[(THF)Mg\{NMe_2BH_2NMe_2BH_3\}_2]$ ($\delta = -15.3, 4.0$ ppm)^{7a} and the scandium species $[Sc(NMe_2BH_2NMe_2BH_3)_2\{N(SiMe_3)_2\}]$ ($\delta = -12.9, 4.0$ ppm),⁵ these latter signals were notably better resolved, as quartet and triplet resonances respectively, than those observed for compound 5; rationalised as a consequence of the greater lability of the group 1 element.

Single crystals of compound 5 suitable for single crystal X-ray diffraction analysis were isolated from a concentrated THF solution at $-30^\circ C$.[†] The results of this analysis are shown in Fig. 1 and selected bond length and angle data are provided in the figure caption. The solid-state structure of 5 may be considered as a dimeric molecule, which assembles as a linear coordination polymer of individual $[K\{NMe_2BH_2NMe_2BH_3\} \cdot THF_2]$ and $[K\{NMe_2BH_2NMe_2BH_3\} \cdot THF]$ units which are propagated by intermolecular $BH_2 \cdots K$ and $BH_3 \cdots K$ multi-centre-bonding interactions. The potassium centres are co-ordinated by the nitrogen atom and further multi-centre-bonding interactions with two boron-bound hydrides of the associated $[NMe_2BH_2NMe_2BH_3]^-$ anion and multi-centre-bonding interactions with boron-bound hydrides of a second $[NMe_2BH_2NMe_2BH_3]^-$ unit, augmented by molecules of THF. The linear coordination polymer which propagates through intermolecular interactions of the BH_3 units with the K atoms of adjacent dimeric units is illustrated in Fig. 2.

Whereas the solid-state structure of compound 5 exhibits some variation in the K–O bond distances, the K1–N1 and K2–N3

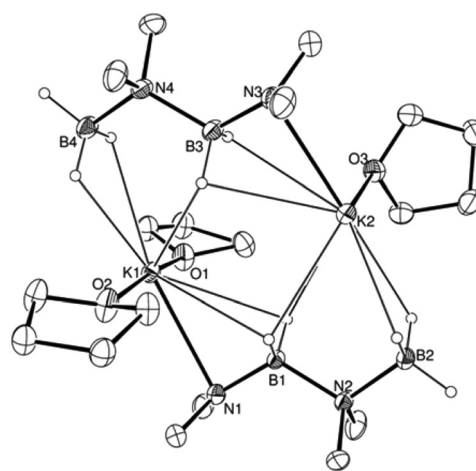


Fig. 1 ORTEP representation of the asymmetric unit of compound 5. Thermal ellipsoids set at 25% probability. Hydrogen atoms other than the boron-bound hydrides removed for clarity. Selected bond lengths (Å) and angles ($^\circ$); K1–N1 2.8726(16), K2–N3 2.8679(17), K1–O1 2.7781(15), K1–O2 2.7448(15), K2–O3 2.7328(16), N1–B1 1.496(3), B1–N2 1.635(2), N2–B2 1.588(3), N3–B3 1.509(3), B3–N4 1.643(3), N4–B4 1.592(3), O2–K1–O2 172.76(5), K1–N1–B1 86.39(10), N1–B1–N2 116.87(16), B1–N2–B2 111.73(14), O3–K2–N3 98.79(5), K2–N3–B3 86.58(11), N3–B3–N4 116.85(17), B3–N4–B4 112.16(15).

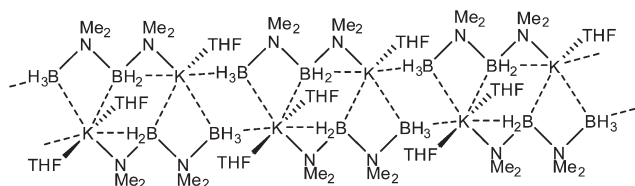


Fig. 2 Propagation of the linear coordination polymer formed by compound 5.

bond lengths are identical within experimental error. The bond lengths of the potassium-bound N–B units [N1–B1 1.496(3), N3–B3 1.509(3) Å] within compound 5 are, however, significantly shorter than those of any previously reported metallated $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion (typically 1.56 Å), whilst the remaining B–N bonds are longer than the corresponding linkages within any previously reported comparable group 2 or group 3 compounds.^{5,7} Although these variations may be rationalised by the adjustment to the identity of the d^0 metal centre, it is likely that the formation of a coordination polymer propagated through multi-centre-bonding interactions between the potassium centres and hydrides of both boron atoms also exerts a significant influence over the precise metrical parameters within the individual $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anions.

Identical reactions performed between $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$ and $[\text{Na}\{\text{N}(\text{SiMe}_3)_2\}]$ with two equivalents of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ at room temperature provided access to the corresponding lithium (6) and sodium (7) $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ derivatives, characterised as quartet and triplet resonances (6: $\delta = -14.7$ ppm $^1J_{\text{BH}} = 89$ Hz and 3.5 ppm $^1J_{\text{BH}} = 98$ Hz; 7: $\delta = -14.7$ ppm $^1J_{\text{BH}} = 87$ Hz and 1.9 ppm $^1J_{\text{BH}} = 98$ Hz) in the respective ^{11}B NMR spectra. Both reactions, however, proceeded markedly more slowly than for the synthesis of compound 5 and neither 6 nor 7 could be isolated in pure form. The formation of the sodium derivative was also accompanied by $[\text{Na}\{\text{NMe}_2\text{BH}_3\}]$, which appeared as a quartet resonance coincidental with the BH_3 unit of 7 in the ^{11}B NMR spectrum.

The similarity of the outcome the stoichiometric reactivity employed in the formation of compounds 5–7 to the species identified as intermediates during the group 2- and group 3-catalysed dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (e.g. 1 and 2)^{5,7} prompted us to assess the activity of the lithium, sodium and potassium bis(trimethylsilyl)amides under catalytic conditions. An initial assessment of the catalytic dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ was, thus, undertaken using 5 mol% of each group 1 reagent in toluene solution. Dehydrocoupling was observed to take place at 80 °C albeit very slowly over the course of 124 hours. In each case the formation of compounds 5–7, comprising ca. 5–10% of the total boron-containing species, was clearly observed in the relevant ^{11}B NMR spectra and the ultimate products of the catalysis were observed to be the cyclic borazane, $[\text{Me}_2\text{NBH}_2]_2$ and a minor quantity of the diamminoborane, $[\text{HB}(\text{NMe}_2)_2]$. We have previously suggested that the production of the latter species is a consequence of a

Table 1 Conversions (%) deduced by integration of ^{11}B NMR spectra for the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ by 5 mol% of the group 1 bis(trimethylsilyl)amides after heating at 80 °C for ca. 124 hours. (mass balance provided by unreacted $\text{Me}_2\text{NH}\cdot\text{BH}_3$)

	$[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$	$[\text{Na}\{\text{N}(\text{SiMe}_3)_2\}]$	$[\text{K}\{\text{N}(\text{SiMe}_3)_2\}]$
$[\text{Me}_2\text{NBH}_2]_2$	72	43	43
$[\text{HB}(\text{NMe}_2)_2]$	5	3	6

β -hydride elimination pathway which is competitive with the δ -hydride elimination required for production of the cyclic borazane (Scheme 1). It is notable, however, that both processes result in the production of the reactive group 1 hydride required for onward reaction with $\text{Me}_2\text{NH}\cdot\text{BH}_3$ within the catalytic manifold. The conversions observed in this qualitative study, summarised in Table 1, indicated that a greater efficacy for the dehydrocoupling reaction is displayed by the smaller lithium centre. Notably the sodium and potassium-based reactions were observed to slow markedly at more advanced reaction times.

To establish the veracity of this apparent trend in reactivity, the reaction kinetics were interrogated by examination of the initial rates of the three reactions between 0.5 mmol $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and 5 mol% of the relevant bis(trimethylsilyl)amide at 50 °C, with the consumption of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ monitored by ^{11}B NMR spectroscopy. The results of these experiments revealed that the initial dehydrocoupling catalysed by the lithium and sodium reagents proceeded at comparable rates, which were intermediate between those previously observed magnesium- and calcium-based catalyses. In contrast the reaction between $[\text{K}\{\text{N}(\text{SiMe}_3)_2\}]$ and $\text{Me}_2\text{NH}\cdot\text{BH}_3$ progressed more slowly and at a rate commensurate with that observed in our previous study of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$.⁷ Although these initial rate data, thus, suggest a trend in reactivity $\text{Mg} > \text{Li} \approx \text{Na} > \text{K} \approx \text{Ca}$, they must be treated with caution as they take no account of other factors at play during more advanced stages of the catalytic reactions. We tentatively ascribe, for example, the lower conversion for the sodium-based reaction (Table 1), which was observed to slow markedly at more advanced stages of the reaction, as a likely consequence of the aggregation of a hydrocarbon-insoluble sodium hydride species.

Conclusions

Group 1 bis(trimethylsilyl)amides act as viable pre-catalysts for the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$. The catalytic reactivity displays similar features to previous reports of dehydrocoupling processes catalysed by d^0 metal centres. The reactions proceed through intermediates containing $[\text{H}_3\text{BNMe}_2\text{BH}_2\text{Me}_2\text{N}]^-$ anions and display a notable kinetic dependence on the identity of the catalytic group 1 reagent, which we suggest is a consequence of variation in charge density of the d^0 centre.

Acknowledgements

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Notes and references

†X-Ray diffraction data for 5. $\text{C}_{20}\text{H}_{58}\text{B}_4\text{K}_2\text{N}_4\text{O}_{34}$, $M = 524.14$, monoclinic, $P2_1/c$, $a = 12.5404(3) \text{ \AA}$, $b = 17.0035(4) \text{ \AA}$, $c = 15.9352(4) \text{ \AA}$, $\beta = 106.6308(12)^\circ$, $V = 3255.74(14) \text{ \AA}^3$, $Z = 4$, $\rho = 1.069 \text{ g cm}^{-3}$, temperature $150(2) \text{ K}$, $R_1 [I > 2\sigma(I)] = 0.0424$, $wR_2 [I > 2\sigma(I)] = 0.0962$, $R_1 [\text{all data}] = 0.0699$, $wR_2 [\text{all data}] = 0.1096$, measured reflections = 61 939, unique reflections = 6385, $R_{\text{int}} = 0.0977$. Crystallographic data for compound 5 are available as CCDC 1043568.

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